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STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

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30 June 1977

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Final Report

COLLISIONAL DISSOCIATION AND STRUCTURAL
PROPERTIES OF ATMOSPHERIC IONS

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Prepared for:


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SRI Project No. 3532

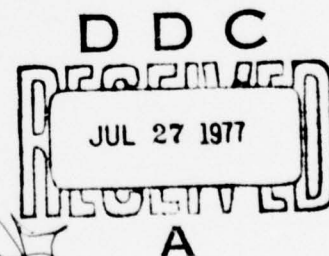
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Approved:


Felix T. Smith, Director

P. J. Jorgensen, Executive Director
Physical Sciences Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The transport properties, collisional dissociation, and photodisso- ciation of N4 ⁺ have been measured. The photodissociation cross section of CO3 ⁻ (CO3(-)) has been interpreted to yield structural information on this ion, including vibrational frequencies, bond energy and electron affinity. A detailed study of the photodissociation of O2 ⁺ (a 4Pi _u) has been made, leading to the discovery of a new state, f 4Pi _g , and of new techniques for high resolution spectroscopy of ions. (F 4Pi(g))		

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INTRODUCTION

In July 1974 we began research on the topic "Collisional Dissociation and Structural Properties of Atmospheric Negative Ions" for the Army Research Office under Contract DAHCO7-74-C-0031. The third year of this research is now complete, and substantial progress has been made. Five publications¹⁻⁵ have resulted from this research, two others^{6,7} are in press, an eighth⁸ has just been submitted, and a ninth⁹ is in the final stages of preparation for publication. Abstracts of the first eight publications are attached. The research results are reviewed in the following section.

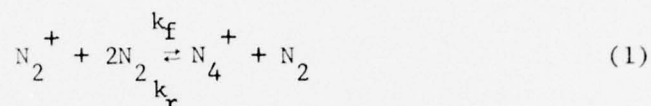
Early in the contract period, the scope of the research was broadened to include positive molecular ions and photodissociative processes. Ions that have been studied during the research are N_4^+ , CO_3^- , O_3^- , and O_2^+ . In these cases significant new results were obtained, and new techniques were developed for the study of the properties of excited states. These new techniques formed the basis for a proposal to ARO to continue research specifically directed toward measurement of the properties of excited states of molecular ions.

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RESEARCH RESULTS

Formation and Collisional Dissociation of N_4^+

At the beginning of this contract we anticipated that the major effort would be directed toward collisional dissociation. We therefore began studies of the reaction

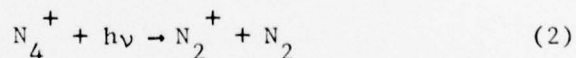


as a test of our analysis techniques. Initial results have been reported at a conference,¹ a more detailed study has been completed, and an article describing the study is in the final stages of preparation for publication.⁹

To summarize, we have determined both the forward and reverse rates from Reaction (1) over the range of E/N from 10 to 150×10^{-17} V cm² (thermal energy to 0.4 eV). The forward rate decreases from 5×10^{-29} to 4×10^{-30} cm⁶/sec over this range, and the reverse rate, collisional dissociation, increases from 6×10^{-15} to 2×10^{-12} cm³/sec.

Photodissociation of N_4^+

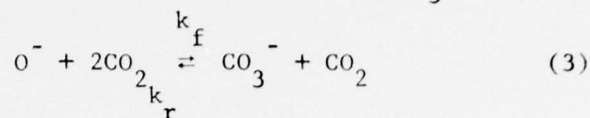
The photodissociation cross section for the reaction



was measured over the wavelength range from 6700 Å to 5400 Å, corresponding to photon energies from 1.85 to 2.30 eV. One motivation for this study was to see if the photoabsorption was characteristic of N_2^+ . Transitions in N_2^+ ($A^2\Pi_u \leftarrow X^2\Sigma_g^+$) exist in this energy range. The photodissociation cross section, however, was observed to increase smoothly from 0.2 to 2.0×10^{-18} cm² over this wavelength range, indicating a transition to a purely dissociative excited state of N_4^+ . A more detailed discussion and interpretation of this work is included in the previously mentioned paper⁹ on N_4^+ .

Collisional Dissociation of CO_3^- and O_3^-

The formation and collisional dissociation of CO_3^-



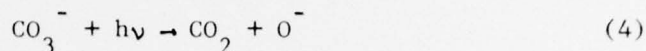
has been investigated. The forward rate was measured over the E/N range from 10 to $120 \times 10^{-17} \text{ V cm}^2$ under other sponsorship and has been reported.¹⁰ Data have been obtained on both the forward and reverse rates up to $500 \times 10^{-17} \text{ V cm}^2$ (2.4 eV), but analysis of these data is not yet complete because of uncertainties in this type of measurement, as discussed in Ref. 9.

Attempts were made to observe the collisional dissociation of O_3^- up to an E/N of $200 \times 10^{-17} \text{ V cm}^2$, but no collisional dissociation was observed. Above this E/N, it was not possible to produce enough O_3^- ions to study the collisional dissociation.

A major but unfortunate result of this work on collisional dissociation was finding that our drift tube is not the most desirable experimental apparatus for determining collisional dissociation rates for ions produced in three-body reactions. Since both the forward rate and the reaction time decrease rapidly with increasing E/N, it is difficult to produce a substantial amount of the product ion at the high E/N values where collisional dissociation is important. These difficulties could have been overcome with rather straightforward modifications of the apparatus, but by the time this was clear, interest in collisional dissociation in the atmosphere had diminished, and therefore, the second aspect of this research program, structural properties of atmospheric ions, was emphasized for the remainder of the contract.

Photodissociation Spectroscopy of CO_3^-

Cross sections for the photodissociation reaction



were obtained under a different ARO contract funded by the U.S. Army Ballistics Research Laboratories for use in ionospheric and stratospheric codes. These cross sections displayed very sharp, detailed structure indicative of a predissociating excited state. Under the current contract and an NSF grant, experiments were performed on the effects of laser polarization and isotopic substitution, and all the results were analyzed to yield significant new information about CO_3^- . An article² describing this work has recently been published; the results are summarized in the attached abstract. The CO_3^- ion is a very important species in the D-region of the ionosphere, and its dissociation by solar photons may have significant effects¹¹ on the ion and electron densities.

Because of our success with CO_3^- , a similar study was made of O_3^- with BRL support. An article¹² describing this study is in preparation.

Photofragment Spectroscopy of O_2^+

Principal Investigator Dr. Moseley spent most of the period from 1 October 1975 to 20 July 1976 at the Université de Paris-Sud in Orsay, France, in the laboratory of Professor Jean Durup. During this period, he was supported primarily by the French Centre National de la Recherche Scientifique, but was partially supported by this contract. His work there was directly related to the goals of this contract.

The major research effort was a study of the photodissociation of the atmospherically important metastable $\underline{a}^4\Pi_u$ state of O_2^+ using techniques of fast beam photofragment spectroscopy. The observed photodissociation was identified as originating with the \underline{a} state, and vibrational levels 4 through 20 were observed. The dissociating state was identified as

$\underline{a}^4 \Pi_g$, and information on the shape of this potential obtained. These results have recently been published³ and are summarized in the attached paper.

During this study we discovered that rotational and fine structure states of the \underline{a} state could be resolved by observing photofragments arising from predissociated levels near the dissociation limit. This new "threshold photofragment spectroscopy" represents a very substantial advance in resolution (more than two orders of magnitude) over normal techniques and has many very interesting implications for the study of ionic states. This new spectroscopy was described in Physical Review Letters⁴ and is summarized in the attached abstract.

Properties of Dissociating States

As a part of the collaboration between Dr. Moseley and Professor Durup and his students, a study was made to summarize ways of using laser photofragment spectroscopy to study dissociating states of molecular ions. For an invited talk at the Seventh International Conference on Mass Spectrometry, an article⁵ was prepared describing the results of this study; an abstract of this article is included with this report. The article discusses precise measurements of the energies of the absorbing levels, determination of individual photodissociation cross sections, information on the potential curve of the dissociating state and on potential barriers giving rise to quasi-bound states, estimation of dissociation or predissociation times on the order of a fraction of a rotation period, evidence for various kinds of predissociation, measurements of branching ratios between fine-structure or vibrational levels of the photofragments, and study of coherent superpositions of dissociating states of different symmetry.

Construction of Photofragment Spectrometer

It is clear from the preceding discussion of the work at Orsay that the techniques of ion photofragment spectroscopy are very well suited to the studies of structural properties of molecular ions. We have just completed construction of a fast ion beam photofragment spectrometer of unique capabilities in order to continue these studies. The construction of this apparatus was supported jointly by the current ARO contract, an AFOSR contract, an NSF grant, and SRI internal funds. An article⁸ describing this apparatus has just been submitted for publication. A preprint of this article is submitted to ARO with this report, and an abstract is attached to this report.

Figure 1 shows the apparatus,⁸ recently constructed at SRI, which can be used for both crossed and coaxial beams photofragment spectroscopy, as well as the high resolution velocity-tuned spectroscopy which will be discussed later. For all these experiments, ions are extracted from an ion source, accelerated to a few thousand volts, and the species to be studied is selected by a mass spectrometer. These parent ions are then collimated to 2 mrad and bent through 90 degrees into the laser interaction region. Here the intracavity photons from a fixed frequency or tunable cw laser can be either coaxial to the ion beam or crossed with it. For photofragment spectroscopy, any photofragment ions produced in the interaction region are bent through 90 degrees and again collimated to 2 mrad so that only photofragments directed along the beam enter the energy analyzer. The energy analyzer is capable of resolving photofragment energies that correspond to about 10 meV in the center of mass. The coaxial beams arrangement is used to maximize the overlap between the photons and ions and is best suited to the study of perpendicular transitions, since the laser polarization is necessarily perpendicular to the beam direction. The crossed beams arrangement can be used to measure the angular distribution of the photofragments by rotating the laser polarization, and to study parallel transitions.

ION SOURCE	FOCUSsing, EXTRACTION, MASS SELECTION	ANGULAR COLLIMATION	LASER INTERACTION	ANGULAR RESOLUTION	PHOTOFRAGMENT ION ENERGY RESOLUTION	AND DETECTION
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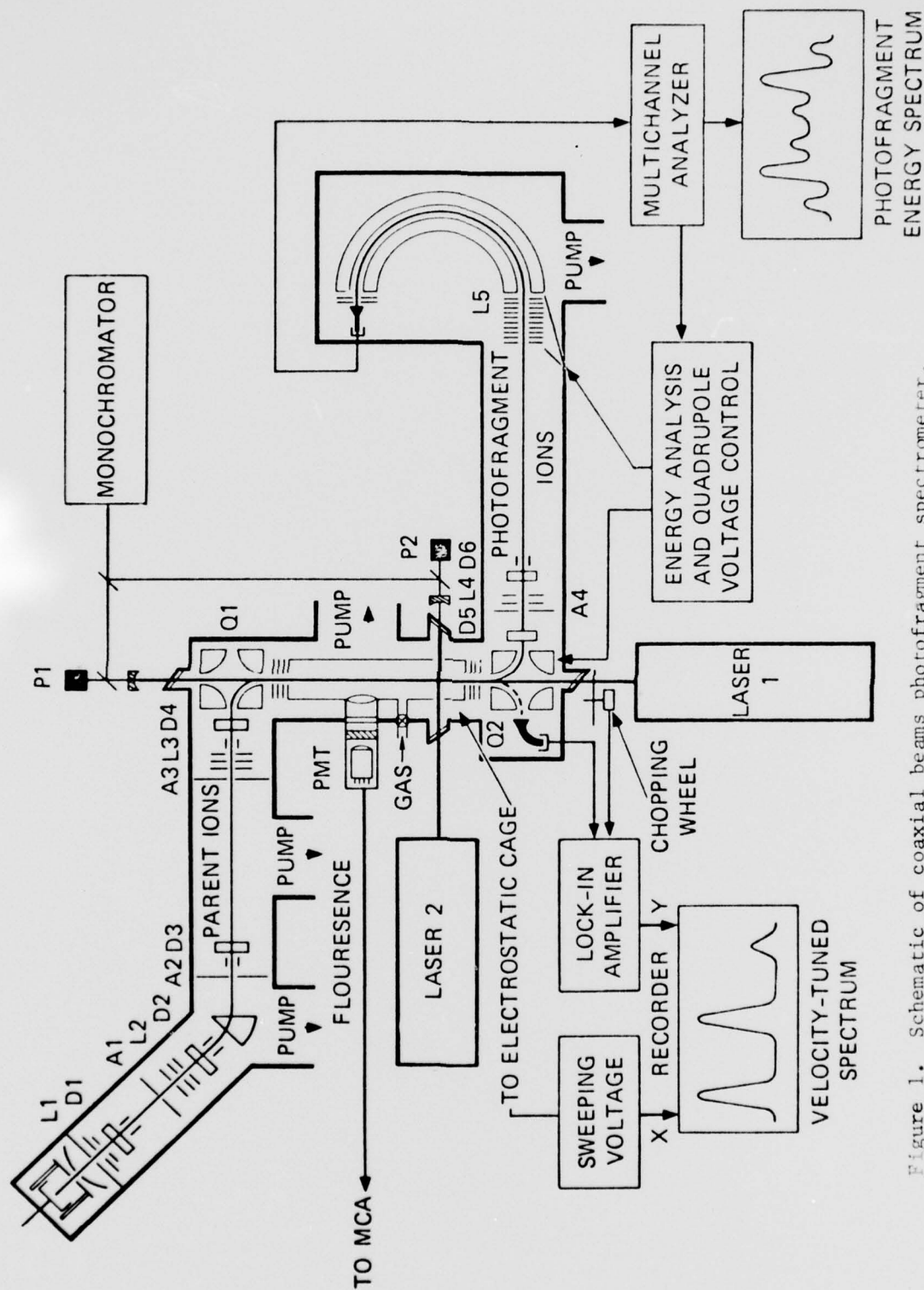
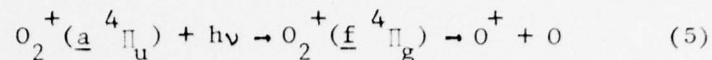


Figure 1. Schematic of coaxial beams photofragment spectrometer.

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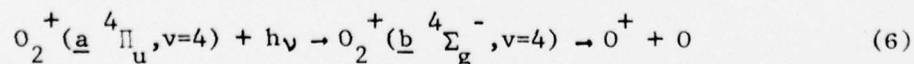
Figure 2 shows a photofragment kinetic energy spectrum for the transition



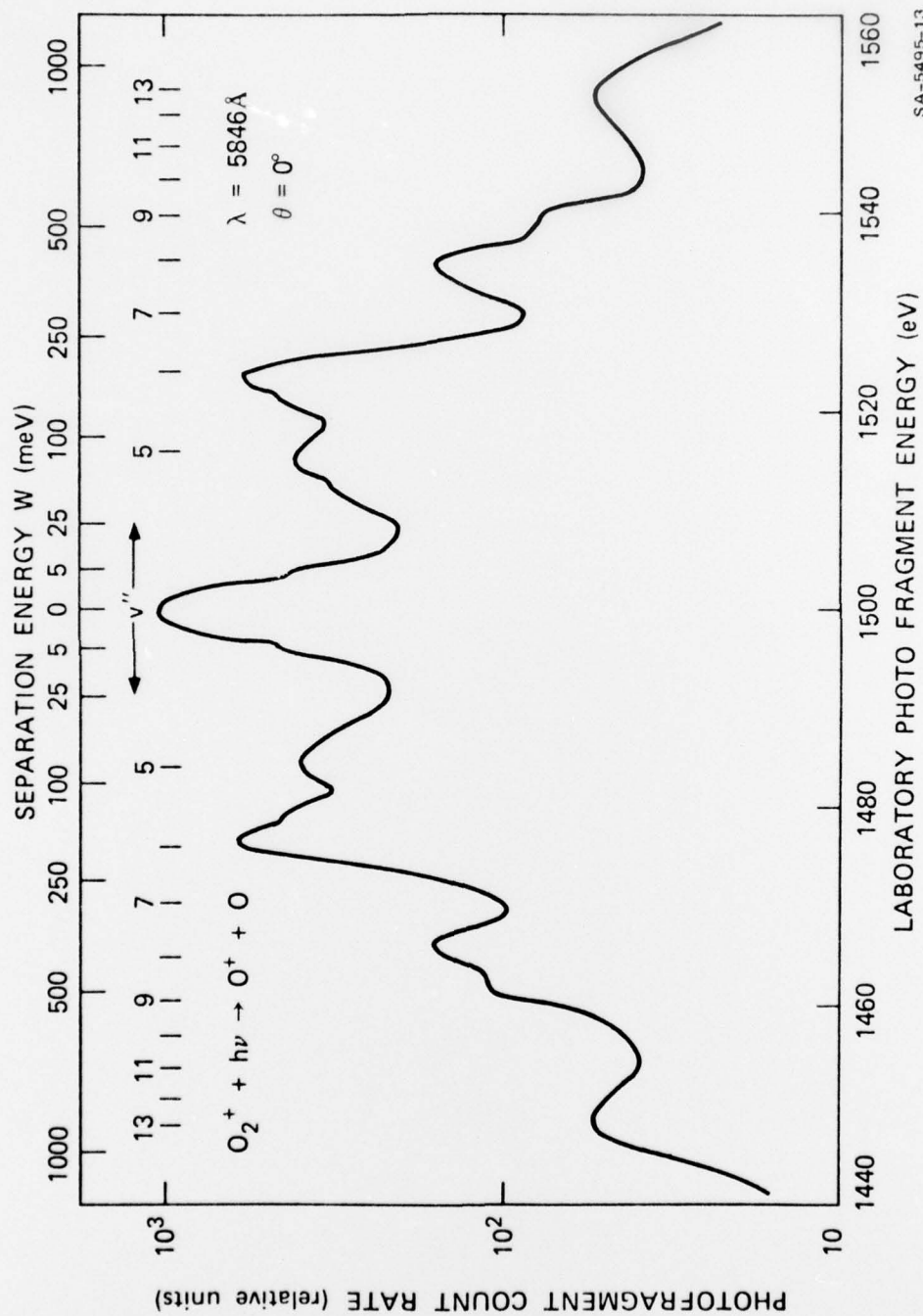
obtained on this apparatus with crossed beams. This transition was studied extensively last year at Orsay,^{3,4} where the $f^4 \Pi_g$ state was observed for the first time, and its general shape and location determined.

The high sensitivity of the apparatus shown in Fig. 5, due to the coaxial beams configuration and use of intracavity laser techniques, has permitted a detailed study¹³ of Ar_2^+ under other sponsorship. This ion is of high fundamental interest and has been the subject of many scattering experiments and calculations. This study resulted in a determination of the $^2\Sigma_u^+$, $^2\Pi_g$, and $^2\Sigma_g^+$ potential curves to an accuracy of about 20 meV, as well as explanation of the effects of the spin-orbit interaction on the potential curves, the magnitude and wavelength dependence of the cross section, and the angular distribution of the photofragments. Similar measurements have been made on Kr_2^+ , and the results are now being analyzed.

Note in Fig. 2 the large photofragment peak at $W = 0$. Since near $W = 0$ the resolution of center-of-mass energies is highest (see upper scale), and the possibility exists for predissociation of the $b^4 \Sigma_g^-$ state and of rotational predissociation of the $f^4 \Pi_g$ state, a study was made of these near-zero energy photofragments as a function of wavelength. This resulted in the discovery⁴ of a strong and highly structured predissociation, where rotational and fine structure levels could be resolved. A small part of this predissociation photofragment spectrum corresponding to the transition

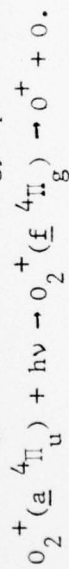


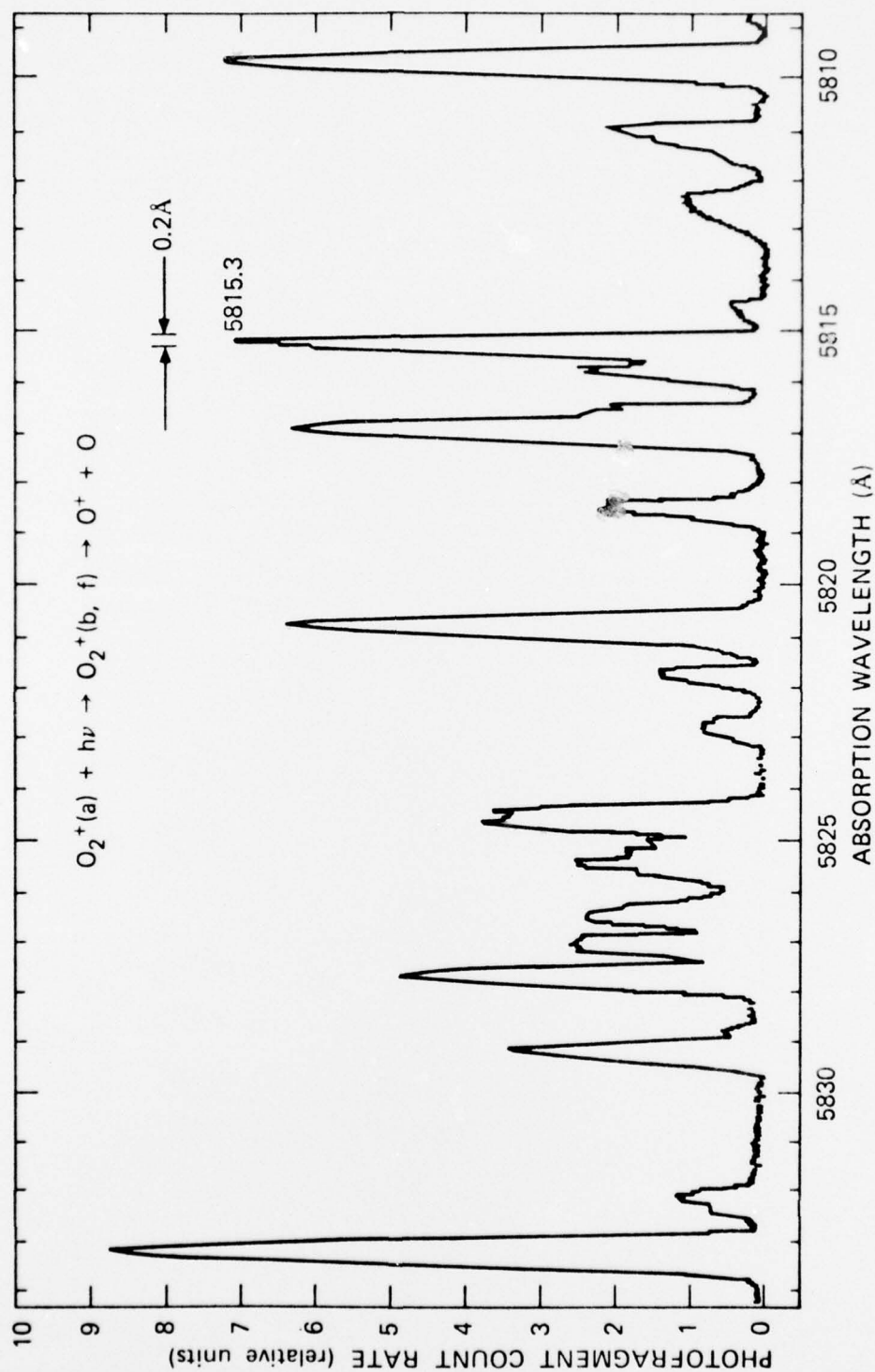
is shown in Fig. 3, where the predissociation is presumably by the f state. At slightly higher photofragment energies around 20 meV, rotationally predissociated levels of the f state appear to be observed directly, and at



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Figure 2. Photofragment kinetic energy spectrum for the transition





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Figure 3. Predissociation photofragment spectrum versus wavelength for the transition $O_2^+ (\bar{a}^4\Pi_u, v=4) + h\nu \rightarrow O_2^+ (\bar{b}^4\Sigma_g^-, v=4)$.

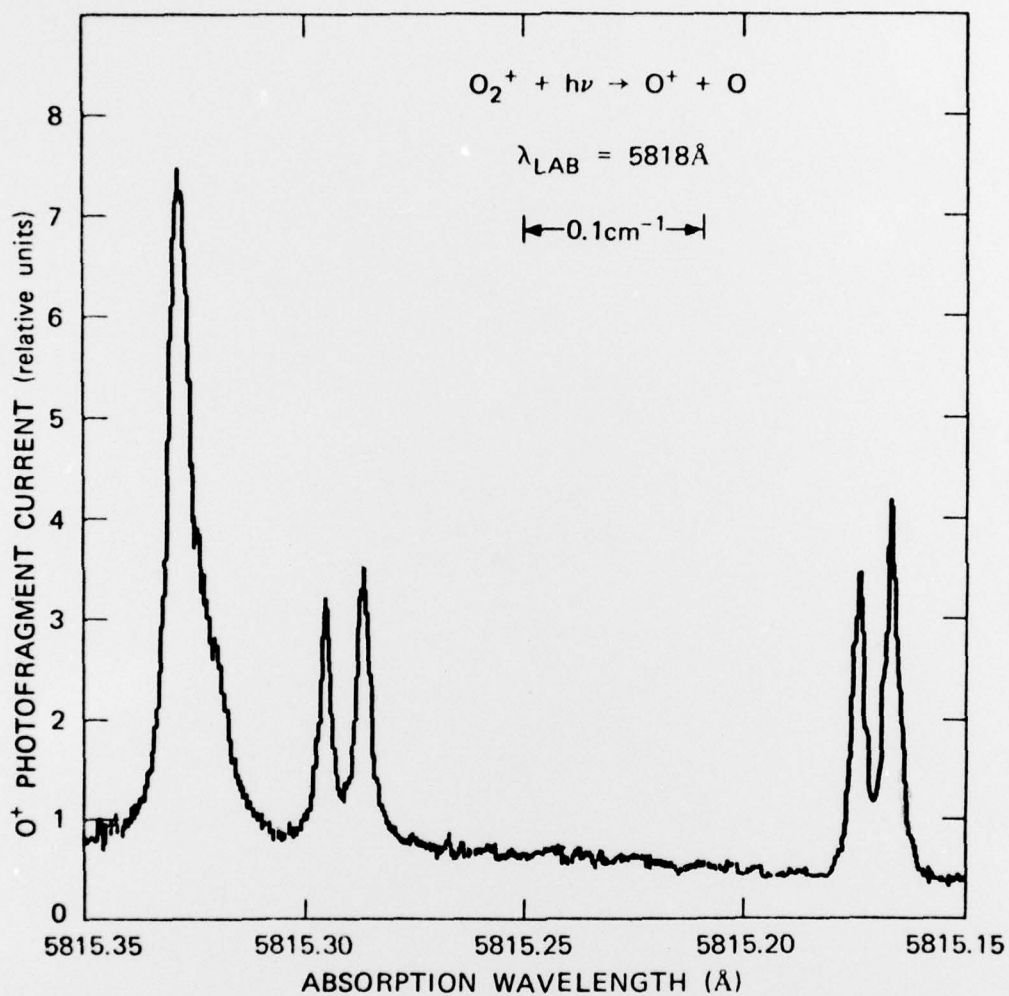
photofragment energies near 90 meV, transitions between the $v = 5$ levels of the a and b states are observed.

In the coaxial configuration, the ions in fast beams can have a very narrow Doppler width for the absorption of laser photons. Fine "tuning" of the absorption wavelengths can be achieved with a fixed laser frequency by varying the ion beam velocity and Doppler-shifting the absorption lines through the laser frequency. This effect was first demonstrated by Wing et al.¹⁴ for vibrational transitions in HD^+ , and has subsequently been observed¹⁵ for electronic transitions in CO^+ and for the transitions (3) in O_2^+ .

An example of a velocity-tuned spectrum is shown in Fig. 4. To obtain this spectrum, the beam energy was swept from 3180 to 3600 eV while the laser was operating at single-frequency near 5818 Å. While the absolute wavelength is uncertain by ± 1 Å, the relative wavelength is precise to within ± 0.0005 Å. The five distinct peaks and the shoulder all lie within the band of 0.2 Å indicated in Fig. 4, and together make up the peak labeled 5815.3. The peak widths in this spectrum vary from 0.7×10^{-6} eV to 2.9×10^{-6} eV, reflecting the lifetime of the predissociating states. This technique should yield measurements of transition energies that are an order of magnitude more precise than existing spectrographic measurements.

The above-described velocity-tuned spectroscopy can also be applied, using the collisional detection scheme of Wing et al.,¹⁴ for both rotational and electronic transitions. This technique has the advantage of not requiring that the transition lead to predissociation, but it requires the use of phase-sensitive detection since a small change in the primary ion current must be observed.

This new spectrometer clearly represents a substantial advance in our ability to study molecular ions. Its capabilities can now be used in the proposed continuation of the work reported here, as well as in ongoing studies sponsored by AFOSR and NSF.



SA-5495-15

Figure 4. Velocity-tuned photofragment spectrum corresponding to the peak indicated by 5815.3 Å in Fig. 3.

CONCLUSION

This three-year research effort has resulted in a substantial increase in our knowledge of dissociative processes in N_4^+ , O_2^+ , and CO_3^- and valuable new information on the excited states of these ions. A unique new coaxial-beams photofragment spectrometer has been constructed, partially supported by this contract, and the capabilities of this new apparatus have been demonstrated. Difficulties were encountered in using the drift tube apparatus to measure collisional dissociation rates, but it is now clear how these difficulties can be overcome. If these rates are needed in the future, they could be determined after making straightforward modifications to our apparatus.

The number of publications, nine, supported fully or in part by this contract is unusually large for a contract of this size. Of course, the work done in Orsay, while directly related to the objectives of this contract, was supported primarily by the France Centre Nationale de la Recherche Scientifique, and the construction of the new apparatus was jointly supported by ARO, AFOSR, NSF, and SRI. Abstracts of each of these publications follow the references.

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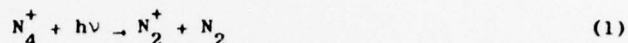
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PHOTON AND COLLISIONAL DISSOCIATION OF N_4^+

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The photodissociation process



has been studied by observation of both the destruction of the parent N_4^+ and of the appearance of the photofragment N_2^+ . The technique is described in two other papers to be presented at this meeting.^{1,2} A tunable dye laser is used to cover the range 5650-6400 Å. The cross section was observed to increase steadily with photon energy in this range. The results are shown in Figure 1.

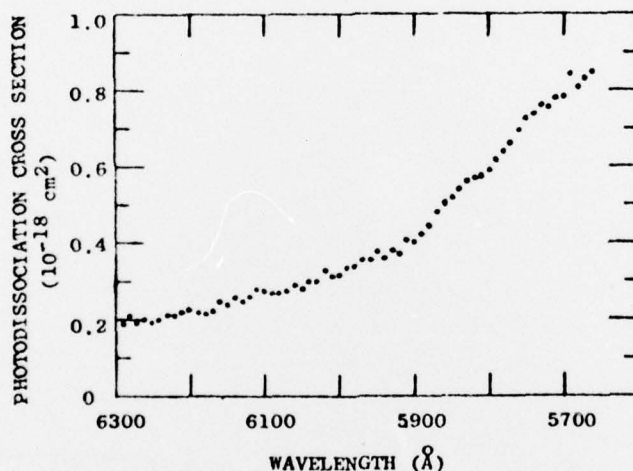


Fig. 1. Photodissociation cross section for N_4^+ . The statistical uncertainty in the points is $< 5\%$. The uncertainty in the absolute scale is about a factor of 2.

We were interested to see if the photon absorption was characteristic of N_2^+ , i.e., is N_4^+ an $N_2^+ \cdot N_2$ cluster? There is a transition $X^2\Sigma_g^+(v=0)$ to $A^2\Pi_u(v=4)$ of N_2^+ in our energy range, at 6124 Å. We did not observe any structure in the cross section; however, the Franck-Condon factor for this transition is only 0.01. All of the photodissociation was observed to be into $N_2^+ + N_2$. Similar measurements on N_3^+ showed no evidence of photodissociation of N_3^+ in our energy range, and no N^+ ions were observed to be created as a result of the photon interactions. We expect to extend the photon energy range of this work.

We are also studying the collisional dissociation of N_4^+ :



which has been previously observed to take place in conventional drift tube apparatuses.³ The N_4^+ bond energy is apparently weak enough that reaction (2) can take place in the drift tube when the ions have a few kT of energy. In our apparatus, the N_4^+ ions can be given an average energy of up to 0.2 eV.

*Supported by the U.S. Army Research Office-Durham.

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2512 The Journal of Chemical Physics, Vol. 65, No. 7, 1 October 1976

Photodissociation spectroscopy of CO_3^-

J. T. Moseley, P. C. Cosby, and J. R. Peterson

Molecular Physics Center, Stanford Research Institute, Menlo Park, California 94025
(Received 6 May 1976)

The photodissociation cross section of gas-phase CO_3^- has been measured over the wavelength range from 4579 to 6940 Å, and reveals detailed structure reflecting the vibrational spacings of a predissociating excited electronic state. From an analysis of the structure, we identified three vibrational modes of the excited state having energies of 990, 1470, and 880 cm^{-1} . The bond energy $D(CO_2-O^-)$ of the ground state CO_3^- was determined to be 1.8 ± 0.1 eV, and the electron affinity of CO_3 was found to be 2.9 ± 0.3 eV. By comparison with theoretical calculations, the lowest predissociating state was identified as 1^2A_1 . Observations regarding other excited states of CO_3^- are made.

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Chemical Physics 17 (1976) 81-89
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LASER PHOTOFRAGMENT SPECTROSCOPY OF O_2^+ : $\tilde{a}^4\Pi_u \rightarrow ^4\Pi_g$

Abdallah TABCHÉ-FOUHAILLÉ, Jean DURUP, John T. MOSELEY,
Jean-Bernard OZENNE, Christiane PERNOT and Mireille TADJEDDINE
Laboratoire des Collisions Ioniques, Université de Paris-Sud, 91405 - Orsay, France

Received 20 April 1976

Translational energy spectra of O^+ ions from photodissociation of $^{16}O_2^+$ and $^{18}O_2^+$ ions by a ruby laser and a flash-lamp pumped tunable dye laser in a crossed-beam experiment are reported. From the observed structure and from its angular dependence the transition is identified as $\tilde{a}^4\Pi_u \rightarrow ^4\Pi_g$, where the upper state belongs to configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2 1\pi_g^3$. The individual vibronic levels whose photodissociation was observed range from $v'' = 4$ to $v'' = 20$ in $^{16}O_2^+$. Some cases were observed where rotational energy was energetically required for photodissociation to occur. Finally, distinct reproducible structure observed in one spectrum is tentatively attributed to the fine structure of the $O(^3P_{0,1,2})$ fragment.

4. Physical Review Letters, Vol. 37, No. 14, page 891, October 4, 1976

High Resolution Threshold Photofragment Spectroscopy of O_2^+ ($a^4\Pi_u \rightarrow f^4\Pi_g$)

J. T. Moseley, M. Tadjeddine, J. Durup, J.-B. Ozenne, C. Pernot, and A. Tabché-Fouhaillé
Laboratoire des Collisions Ioniques, Université de Paris-Sud, 91405 Orsay, France
(Received 20 July 1976)

A new technique of laser photofragment spectroscopy is introduced and applied to a study of transitions from the $v = 4$ level of the $a^4\Pi_u$ state of O_2^+ to predissociating levels of the $f^4\Pi_g$ state near the dissociation limit. A resolution of 0.5 MeV is obtained, and specific (M, J) levels of the a state are identified. Much higher resolution is possible.

5. Advances in Mass Spectrometry 7, in press.

Dissociating States of Molecular Ions Studied
by Laser Photofragment Spectroscopy

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ABSTRACT

On the basis of our current experimental and computational work on laser photofragment spectroscopy of molecular ions, including threshold photofragment spectroscopy, we discuss the kind of data which may be obtained by these methods. They include precise measurements of the energies of the absorbing levels, determination of individual photodissociation cross sections, information on the potential curve of the dissociating state and on potential barriers giving rise to quasi-bound states, estimation of dissociation or predissociation times in the order of a fraction of a rotation period, evidence for various kinds of predissociation, measurements of branching ratios between fine-structure or vibrational levels of the photofragments, and study of coherent superpositions of dissociating states of different symmetry.

6. Review of Scientific Instruments, in press.

DEFLECTION OF AN ION BEAM IN THE TWO-DIMENSIONAL
ELECTROSTATIC QUADRUPOLE FIELD

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ABSTRACT

The theory behind the use of a two-dimensional quadrupole field as an ion beam deflector is discussed. The design of such a deflector for merging an ion beam with an ion beam of the opposite charge, with a neutral atomic beam, or with a laser beam is described. A deflector that has been built and tested is described. It can deflect a 3 kV ion beam of 2 mm diameter, ± 2 mrad angular spread, and 1 eV FWHM energy spread, by 90° without causing a detectable increase in the diameter or angular spread of the beam.

7. To be published in ELECTRONICS AND ATOMIC COLLISIONS, Abstracts of Papers of the X ICPEAC, Paris, 1977.

THRESHOLD PHOTOFRAGMENT SPECTROSCOPY OF $O_2^+(a^4\Pi_u)^*$

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Threshold photofragment spectroscopy of the metastable $a^4\Pi_u$ state of O_2^+ , originated last year at Orsay,¹ has been applied with an order of magnitude higher resolution, revealing even more detailed structure than had been predicted. With this technique, one investigates photodissociations near the threshold which result in near zero energy photofragments. These photodissociations can be due to a repulsive potential, to quasi-bound levels (such as in rotational predissociation), or to the predissociation of a bound state. For predissociations, the resolution depends only on the lifetime of the dissociating level and the linewidth of the laser. The characteristics of the photofragment spectra versus kinetic energy and wavelength allow the dissociating state to be identified, and levels of both initial and final predissociating states determined.

The measurements were performed using a new coaxial-beams photofragment spectrometer² and a cw dye laser with a line width of about 0.2 Å. A part of the spectrum versus wavelength for a photofragment energy of 0 ± 1 meV is shown in Fig. 1. The photon energy required to dissociate the $v=4$ level of the a state from the center of the four fine structure levels with no rotational energy to the

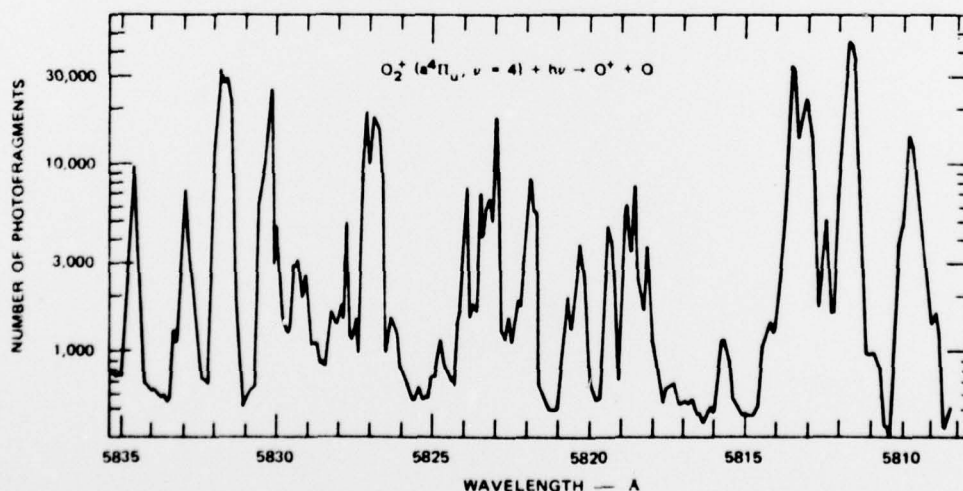


Figure 1. Threshold photofragment spectrum of $O_2^+(a^4\Pi_u) + h\nu$.

lowest dissociation limit ($O^+(^4S_0) + O(^3P_2)$) corresponds to 5791 Å. Peaks are separated with a resolution of 0.05 meV. Spectra such as that shown in Fig. 1 have been obtained over the wavelength range from 5760 to 5900 Å, for 11 dissociation separation energies between 0 and 300 MeV. In addition, spectra in kinetic energy have been obtained at the wavelengths corresponding to each major peak in the wavelength spectra. Although analysis of these data is not yet complete, some conclusions can be drawn. First, there are too many transitions to be explained by only the previously proposed¹ dissociation of quasi-bound levels of the $f\ ^4\Pi_g$ state. Second, the transitions appear to be grouped in three photofragment energy ranges: 0-10 meV, 15-25 meV, and 90-100 meV. A preliminary analysis suggests that the first energy group corresponds to the transition $\underline{b}\ ^4\Sigma_g^-(v=4) \rightarrow \underline{a}\ ^4\Pi_u(v=4)$; the second to $\underline{f}\ ^4\Pi_g \rightarrow \underline{a}\ ^4\Pi_u(v=4)$; the third to $\underline{b}\ ^4\Sigma_g^-(v=5) \rightarrow \underline{a}\ ^4\Pi_u(v=5)$.

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¹ J. T. Moseley, M. Tadjeddine, J. Durup, J.-B. Ozenne, C. Pernot and A. Tabché-Fouhaillé, Phys. Rev. Lett. 37, 891 (1976).

² B. A. Huber, T. M. Miller, H. D. Zeman, R. L. Leon, P. C. Cosby, J. T. Moseley, and J. R. Peterson, "A Laser-Ion Coaxial Beams Spectrometer," submitted to Rev. Sci. Instr.

8.

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A LASER-ION COAXIAL BEAMS SPECTROMETER

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ABSTRACT

An apparatus has been designed and constructed to provide laser excitation of ion beams in both coaxial and crossed-beam configurations. The coaxial geometry provides very high sensitivity and nearly Doppler-free wavelength resolution for spectroscopic measurements, and allows the use of the Doppler shift to "tune" the wavelength. A novel transverse quadrupole electric field arrangement is used to deflect the ion beam into and out of the laser beam axis. The ion beam is highly collimated and a high resolution 180° electrostatic analyzer is used for photofragment energy analysis. The apparatus has demonstrated a resolution of better than 10 meV for normal photofragment spectroscopy, and 0.001 meV for coaxial beams photofragment spectroscopy using a single-mode laser. While providing these high resolutions the apparatus has an overall sensitivity several orders of magnitude greater than conventional ones.